STRETCHABLE AND TRANSPARENT SILICONE/ZINC OXIDE NANOCOMPOSITE FOR ADVANCED LED PACKAGING

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STRETCHABLE AND TRANSPARENT SILICONE/ZINC OXIDE NANOCOMPOSITE FOR ADVANCED LED PACKAGING

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LIST OF SYMBOLS AND ABBREVIATIONS

E	Elastic modulus
σ_{max}	Maximum stress
LED	Light-emitting diode
RI	Refractive index
UV	Ultraviolet
XRD	X-ray diffraction

SUMMARY

At present, one of the key challenges in the light-emitting diode (LED) packaging technology is light extraction due to the difference in index of refraction between LED chip and air. Silicone nanocomposites have been extensively researched for applications in LED encapsulant to reduce such difference in refractive index. It is well-known that silicone is desirable for LED encapsulant because of its optical transparency and photothermal resistance. However, not much has been accomplished to leverage the elastic properties of silicone for enabling a stretchable LED encapsulant. In this work, I aim to investigate the stretch ability of silicone/zinc oxide (ZnO) nanocomposites for LED packaging. Wurtzite ZnO nanoparticles were prepared in colloids and subjected to silane treatment. Effects of both *ex situ* and *in situ* silane treatment on the final mechanical and optical properties of the silicone/ZnO nanocomposites were examined. Silicone/ZnO nanocomposites exhibit significantly more compliant stress-strain behavior than silicone control. In particular, silicone/silane-treated ZnO nanocomposites show more serrated stress-strain curves. They also embrace higher transmittance than silicone/unmodified ZnO nanocomposites, indicating an improvement in the dispersion of the nanoparticles. It was found that the silicone/5% silane-treated ZnO nanocomposite prepared by an *in situ* method was able to deform over a range of up to 160%. The film made of this unique silicone/ZnO nanocomposite (~40 microns thick) exhibits transmittance >70% throughout the visible range.

CHAPTER 1

INTRODUCTION

In high power light-emitting diode (LED) packaging, light extraction is the primary focus of LED encapsulation, and ultimately has a direct impact on device efficiency [1]. Low light extraction efficiency results from a difference in the refractive index (RI) between the air and the LED chip which narrows the light escape cone [2]. An effective approach to improving light extraction efficiency is to reduce the difference in index of refraction by incorporating high-RI nanoparticles (NPs) into optically clear polymer encapsulant. For example, epoxy resins [3] and silicone [4] have been widely used in recent studies to prepare the polymer matrix of LED encapsulant. On the other hand, nano zinc oxide (ZnO) [2], titania [5], zirconia [6], etc. have been used as fillers of the polymer encapsulant to further increase refractive index.

Silicone is a transparent elastomer that consists of silicon-oxygen bonded backbones which form a three-dimensional network after being cured through interchain covalent bonding, as shown in Figure 1. This unique network structure prevents the polymer chains from slipping past one another under a load, and hence the restricted mobility of the chains makes the material elastic. In the past, the characteristics of silicone, such as high transparency and photothermal resistance, have received significant attention to develop desired properties of LED encapsulant. However, not much work has been done with regards to the elastic properties of silicone for realizing its potential as a stretchable LED encapsulant.

Figure 1 Three-dimensional network structure of cured silicone

ZnO is a non-toxic and cost-effective semiconductor with high refractive index of 2.0 [7]. It is anticipated that the inclusion of nano ZnO would increase the refractive index of the silicone-based encapsulant beyond its limit of 1.45-1.55 [2]. Sun et al. reported synthesis of colloidal ZnO nanoparticles by hydrolyzing zinc acetate dihydrate in basic methanol solution, followed by a precipitation-redispersion washing procedure to purify the nanoparticles [8]. In this work, we adopted the above approach to prepare the nanofiller of the silicone-based encapsulant.

It is challenging to incorporate dried nanoparticles into the polymer matrix because of the possibility to formulate aggregation of the particles and ultimately impair transparency of the nanocomposites. Whereas solution mixing is a direct dispersion method [3] to reduce particle agglomeration in the polymer matrix, this approach requires the particles to be uniformly dispersed in a solvent that is miscible with the polymer matrix [9]. In the case of ZnO nanoparticles, they are precipitated from the basic methanol solution with a surrounding layer of hydroxyl groups that are incompatible with the silicone matrix. As a result, phase separation between polymer and nanofiller can still occur after solvent extraction. One potential solution is to perform silane treatment for modifying the surface of the ZnO nanoparticles by reacting with the hydroxyl groups and

coating the nanoparticles with alkyl groups to stabilize the nanoparticles. In this work, the silane-treated ZnO nanoparticles are dispersed in toluene that is miscible with silicone. The highly volatile characteristic of toluene allows solvent evaporation to remove it readily.

CHAPTER 2

LITERATURE REVIEW

LEDs have advantages over the existing incandescent and halogen lamps in terms of power efficiency, reliability, and lifetime [10]. The LED is a semiconductor device that converts electrical energy into light by a recombination process of electrons and holes. Once light is generated, it has to get out of the device and travel through the air, before reaching our eyes. Refraction occurs when there is change in the medium the light is traveling through. In the case of LED, the refractive angle is larger than the incident angle because air is a less dense medium than the LED chip. If the incident angle exceeds a critical value, total internal reflection occurs with some light bouncing back instead of exiting the chip. The light bounced back is then trapped, limiting the light extraction efficiency of LED. To combat this issue, the LED lamp is encapsulated with materials having index of refraction larger than that of air as a solution to lessen the refractive index mismatch and to widen the light escape cone.

Polymer Encapsulant

Existing literature has cited extensive research with efforts to reduce the difference in index of refraction. In standard LED technology, epoxy resins are typically employed as encapsulant materials due to their visible transparency, good adhesion, and high glass transition temperature [3]. However, it is argued that a major disadvantage of epoxy resin arises from the discoloration under ultraviolet (UV) irradiation. This is attributed to the aromatic ring in the epoxy resin which easily absorbs UV light and leads to chain scission [11]. Alternatively, the UV-resistant silicone serves as a potential replacement for epoxy resin in LED devices [4]. In the past, the perfect visible transparency and resistance to photothermal degradation of silicone have received

attention as the highlighted desirable properties of LED encapsulant [1], whereas the elastic properties of silicone were underestimated. In fact, the flexibility of silicone LED encapsulant could lead to promising applications in stretchable electronics.

Silicone is a kind of transparent elastomer that consists of silicon-oxygen bonded backbones. Current research on silicone polymer chemistry and structure has given rise to different types of silicones within a broad spectrum of compositions [4]. Silicone gels contain reactive silicone polymers and reactive silicone cross-linkers in a two-part system. When two parts are combined and cured, the resulting material is soft, compliant, and sticks to the substrate without migrating [12]. These attributes make silicone a viable candidate for LED encapsulant. Another advantage of silicone chemistry is the wide variety of cure systems available including UV, condensation, and addition types [13]. In LED packaging, the dominant cure system of silicone is thermal curing at moderate temperatures, which makes it easy to process. However, there is an intrinsic limitation of silicone: the refractive index of silicone is usually limited to 1.45 to 1.55 [2], which is much lower than the refractive index of 2.5-2.7 for a common LED chip made from gallium nitride [12]. In order to reduce the RI mismatch and improve the light extraction efficiency of LED, the refractive index of encapsulation materials has to be increased to a greater extent.

Zinc Oxide Nanoparticles

To further improve light extraction efficiency, much effort in the recent decades has been devoted to incorporating high-RI inorganic nanoparticles into polymer matrix to make polymer/inorganic nanocomposite LED encapsulants. Literature regarding the filler of nanocomposite LED encapsulant has indicated a great number of studies with their focuse on the incorporation of ZnO nanoparticles into the polymer matrix. Nano ZnO is a very promising semiconductor due to its nontoxicity, low cost, and chemical stability towards air. Its wide band gap (3.37 eV) makes it completely transparent in the visible

spectrum [7]. Since the refractive index of ZnO is 2.0 at a wavelength of 589 nm, the refractive index of silicone/ZnO nanocomposite is expected to increase upon addition of ZnO nanoparticles. Liu et al. [2] suggested that particle size be controlled smaller than one tenth of the visible light wavelength (400-700 nm) in order to reduce Rayleigh scattering and maintain transparency of the nanocomposite. As reported by Sun et al. [8], ZnO nanoparticles with sizes ranging from 2 to 5 nm were synthesized by hydrolyzing zinc acetate dihydrate in basic methanol solution, followed by a precipitation-redispersion washing procedure to purify the nanoparticles. The concentration of inorganic ions in the suspension of nanoparticles was shown to be dramatically reduced by the washing. Therefore, I adopted the synthesis and purification methods reported by Sun et al. to prepare ZnO nanoparticles in this work.

Polymer/Inorganic Nanocomposites

Although there is existing research stating that introduction of inorganic components can greatly enhance performance of polymer nanocomposite in terms of mechanical, electronic, thermal, and optical properties [7], other studies raise the concern of nanoparticle aggregation that may result in the opaqueness of nanocomposite. Yang et al. [3] claimed that incorporating dried nanoparticles into polymer matrix would easily lead to aggregation of nanoparticles and would readily bring about opaqueness of the nanocomposite even at nanofiller content of less than 0.5 weight percent. Therefore, Yang et al. [3] reported for the first time a direct dispersion solution mixing method by dispersing suspension of ZnO quantum dots without drying in epoxy resin to alleviate nanoparticle aggregation and achieve better dispersion. Since then, this method has been extensively adopted in fabrication of nanocomposites. But Sun et al. [9] pointed out a constraint of this straightforward approach; it requires the particles to be dispersed in a solvent that is also miscible with the polymer matrix. Sun et al. [9] also stated that even if this preliminary criterion is satisfied, phase separation between the polymer and

nanofiller can still occur after solvent extraction. In addition, Liu et al. [2] expressed the view that the micro air bubbles generated by the remaining solvent in the polymer matrix during the curing process could decrease the refractive index of the nanocomposite. It can thus be concluded that this direct dispersion solution mixing method can reduce nanoparticle aggregation, while imposing new challenges on the solvent evaporation process.

CHAPTER 3

EXPERIMENTAL PROCEDURE

Figure 2 shows the experimental steps involved in the fabrication of silicone/ZnO nanocomposite. The chemicals were purchased from VWR International and directly used without further processing.

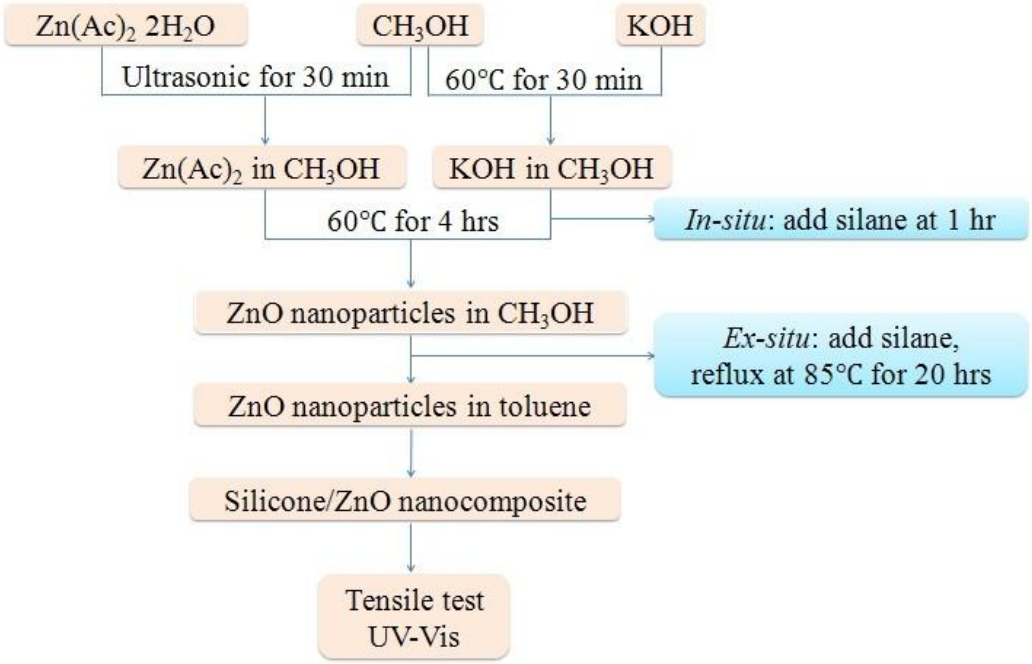

Figure 2 Fabrication process of silicone/ZnO nanocomposite

Synthesis of ZnO Nanoparticles

7 mmol zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$) in 50 mL methanol (CH_3OH) solution was placed in Branson 3510 ultrasonic cleaner for 30 min; 14 mmol potassium hydroxide (KOH) in 150 mL methanol solution was oil-bathed at 60 ℃ with constant magnetic stirring for 30 min. Both solutions were then mixed and oil-bathed at 60 ℃ with constant magnetic stirring at 500 rpm for 4 hours.

Purification of ZnO Nanoparticles

The suspension of nanoparticles was concentrated by means of rotary evaporation at 55 ℃ under vacuum. Isopropyl alcohol and hexane were added at a ratio of 1:5 to the concentrated suspension. Subsequently, the mixture was left to sit in the fridge for at least 10 hours and the supernatant was removed. After the above process was repeated three times, the concentrated suspension of nanoparticles was centrifuged at 5000 rpm for 15 min and redispersed in toluene.

Silane treatment by *ex situ* and *in situ* methods

ZnO nanoparticles were stabilized through surface modification by coating them with (3-chloropropyl)triethoxy silane. In the *ex situ* method, ZnO nanoparticles were first prepared in methanol and concentrated via rotary evaporation. The silane solution was then added in 1 weight percent, followed by refluxing at 85 ℃ for 20 hours with constant magnetic stirring.

In the *in situ* method, the preparation of ZnO nanoparticles was basically the same, except that the silane solution was added to the reaction mixture ($Zn(Ac)_2$ and KOH in methanol) when the mixture had been baked for 1 hour. The silane-treated ZnO nanoparticles were then centrifuged and redispersed in toluene.

Fabrication of Silicone/ZnO Nanocomposites

The toluene suspension of ZnO nanoparticles was added to Sylgard 184 silicone elastomer (silicone 184) base at 5 weight percent. Toluene solvent was evaporated at room temperature under atmospheric pressure with constant magnetic stirring. After the curing agent was added at a ratio of 1:10 to the base, the nanocomposite was either pipetted to fill the tensile test mold or spin-coated onto a glass substrate. The nanocomposite was cross-linked through thermal curing at 150 ℃ for 10 minutes.

Characterization

Uniaxial tensile tests were performed using Instron Microtester 5548 at room temperature. Transmittance measurements were carried out using a Shimadzu UV-2450 spectrophotometer. The crystallinity of ZnO nanoparticles was characterized using X-ray diffraction (XRD). Thickness of the nanocomposite films was measured using Heidenhain ND 281 B display unit.

CHAPTER 4

RESULTS AND ANALYSIS

Figure 3 shows the UV-vis spectra of the reaction mixture at 0 and 1 hr, respectively. The clear peak between 300 and 350 nm is assigned to the electronic transition from top of the valence band to bottom of the conduction band. The absorption peak demonstrates an evident blue shift when compared with the peak of bulk ZnO (at 373 nm), suggesting that the particles are in the quantum regime [14]. Pesika et al. found that the shape of the absorption spectrum for a suspension of quantum particles could reflect the particle size distribution [15]. Hence, the sharp absorption edge and prominent peak position, as shown in Figure 3 at 1 hr, indicates the narrow size distribution of ZnO nanoparticles.

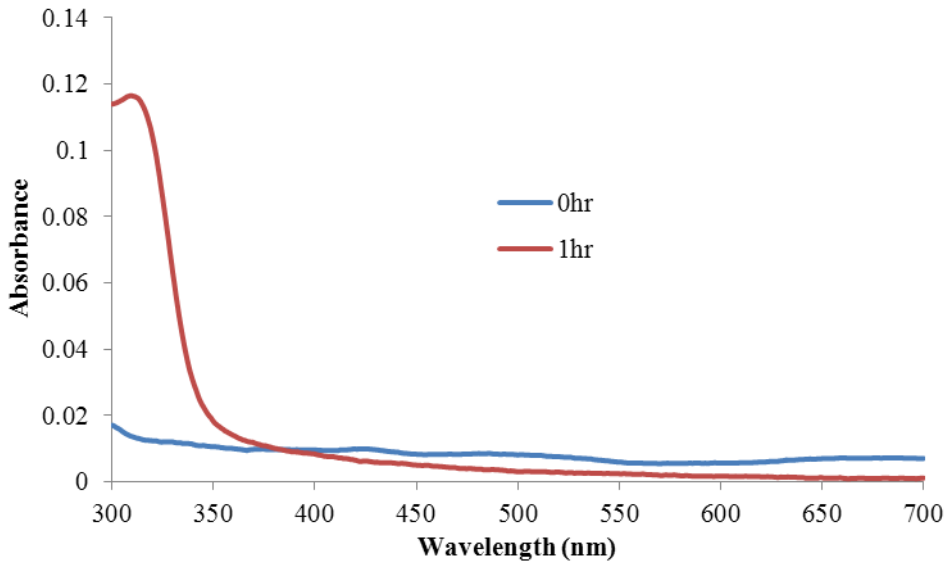

Figure 3 UV-Vis spectra of the reaction mixture at 0 and 1 hr

Figure 4 gives the XRD profile of ZnO nanoparticles without surface modification is demonstrated in Figure 4. The diffraction peaks are attributed to the presence of hexagonal wurtzite crystallites.

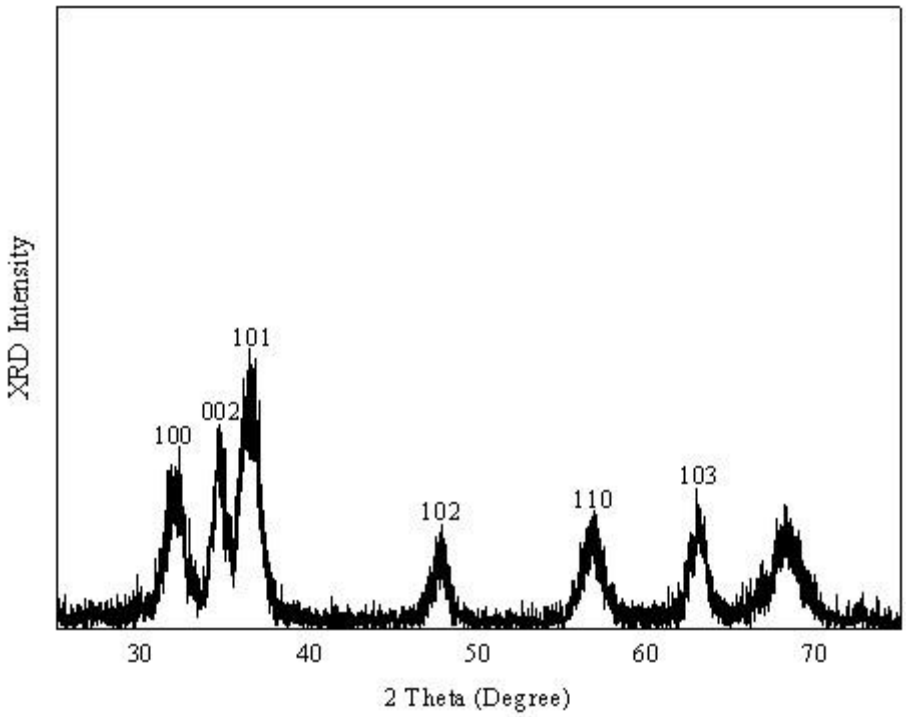

Figure 4 XRD profile of ZnO nanoparticles without surface modification

Figure 5 presents the stress-strain curves of silicone 184 control and silicone 184/5% unmodified ZnO nanocomposite before failure. Silicone 184 control exhibits nonlinear stress-strain behavior which is characteristic of an elastomer. In contrast, silicone 184/5% unmodified ZnO nanocomposite shows linear stress-strain behavior and lower stiffness. These results are consistent with previous findings. For example, Hertz suggested that addition of fillers to an elastomer automatically puts the network under strain [16]. Qi and Boyce also pointed out that a pre-stretched material exhibits a significantly more compliant response than that of the virgin material [17].

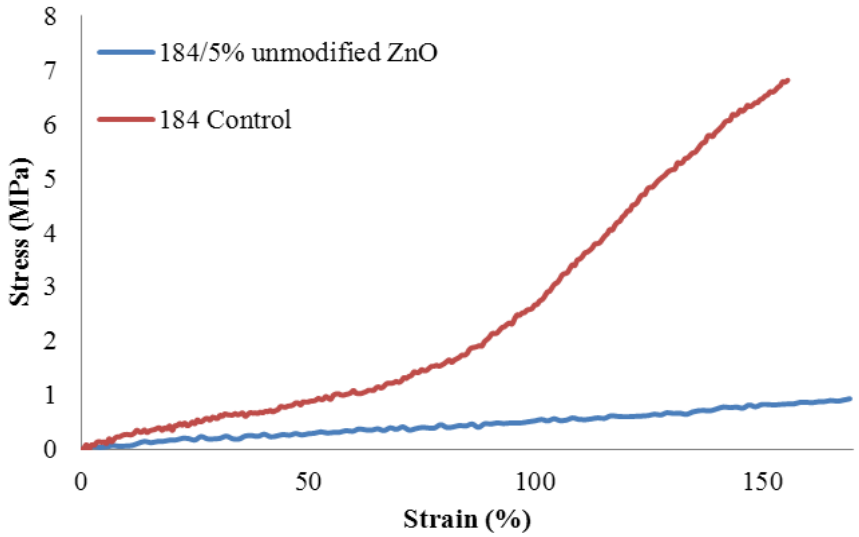

Figure 5 Stress-strain curves of silicone 184 control and silicone 184/5% unmodified ZnO nanocomposite before failure

Figure 6 shows the stress-strain curves of silicone 184 control and silicone 184/5% silane-treated ZnO nanocomposites before failure, respectively. Silicone 184/5% silane-treated ZnO nanocomposites exhibit more serrated stress-strain behavior than silicone 184 control, indicating inhomogeneous deformation.

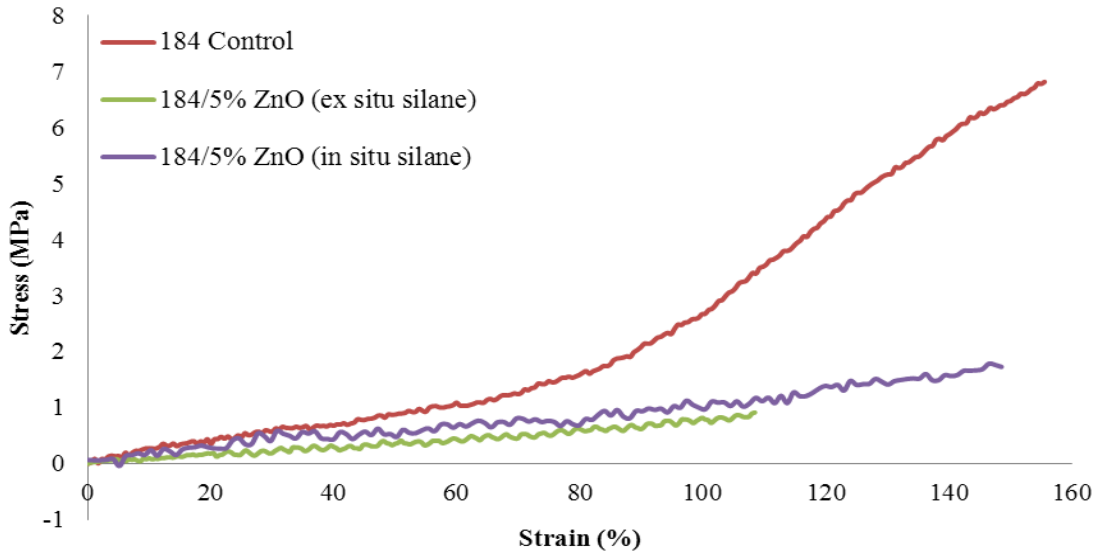

Figure 6 Stress-strain curves of silicone 184 control and silicone 184/5% silane-treated ZnO nanocomposites before failure

Figure 7 shows the breaking strains of silicone 184 control and silicone 184/5% ZnO nanocomposites. Silicone 184/5% silane-treated ZnO nanocomposite using *ex situ* method exhibits lowest breaking strain of 107%. Silicone 184 control and the other two silicone 184/5% ZnO nanocomposites can deform over a wider range of up to 160%.

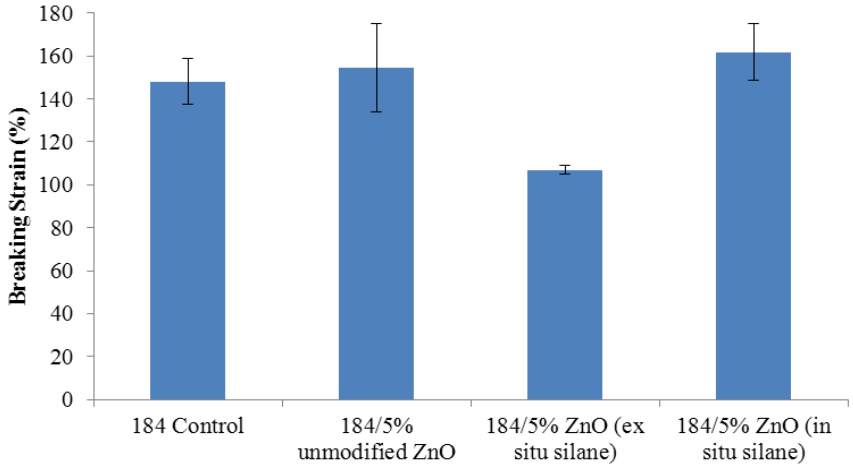

Figure 7 Breaking strains of silicone 184 control and silicone 184/5% ZnO nanocomposites

Figure 8 shows the maximum stresses of silicone 184 control and silicone 184/5% ZnO nanocomposites. Silicone 184 control is able to achieve maximum stress of 6.5 MPa. Silicone 184/5% ZnO nanocomposites, however, break at much lower stress.

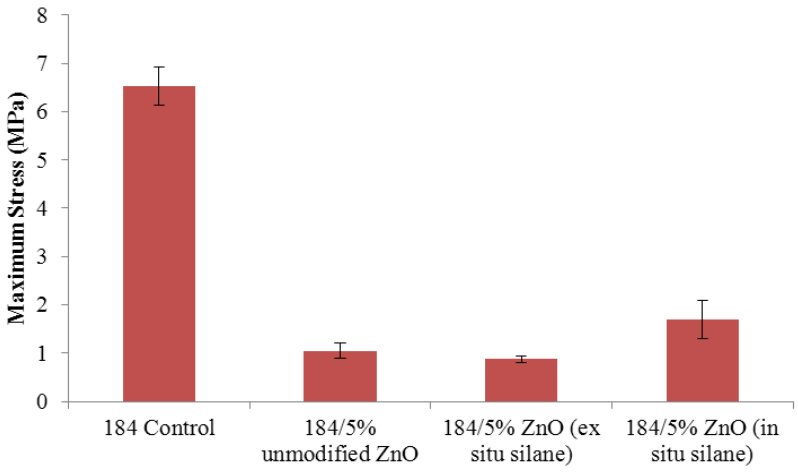

Figure 8 Maximum stresses of silicone 184 control and silicone 184/5% ZnO nanocomposites

The elastic moduli of silicone 184/5% ZnO nanocomposites are shown in Figure 9. Table 1 displays the maximum stress to elastic modulus ratio (σ_{max}/E) of silicone 184/5% ZnO nanocomposites.

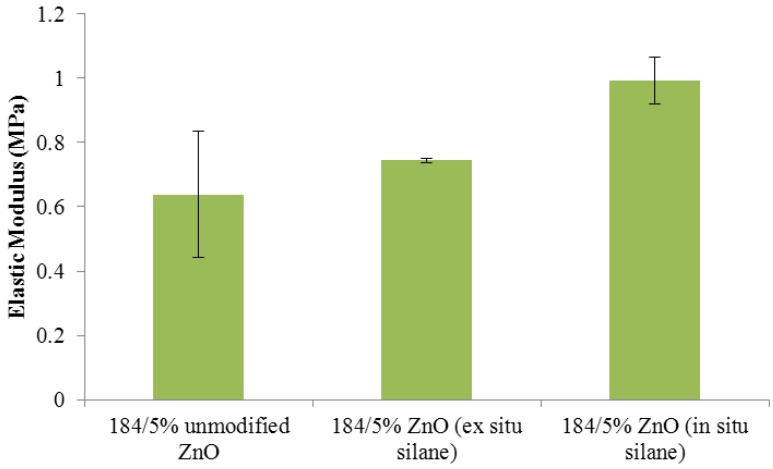

Figure 9 Elastic moduli of silicone 184/5% ZnO nanocomposites

Table 1 Maximum stress to elastic modulus ratio of silicone 184/5% ZnO nanocomposites

Nanocomposite	σ_{max}/E
Silicone 184/5% unmodified ZnO	1.644
Silicone 184/5% silane-treated ZnO (*ex situ*)	1.172
Silicone 184/5% silane-treated ZnO (*in situ*)	1.707

Figure 10 displays the transmittance spectra of silicone 184 control and silicone 184/5% ZnO nanocomposite films in the visible range. The silicone/silane-treated ZnO nanocomposite films embrace higher transmittance in the visible range than the silicone/unmodified ZnO nanocomposite film, which indicates less particle agglomeration. Silane treatment reduces the polarity of ZnO nanoparticles by replacing the surrounding hydroxyl groups with alkyl groups. The reduced polarity makes the particles split more easily with agitation, thereby breaking down agglomerates [18].

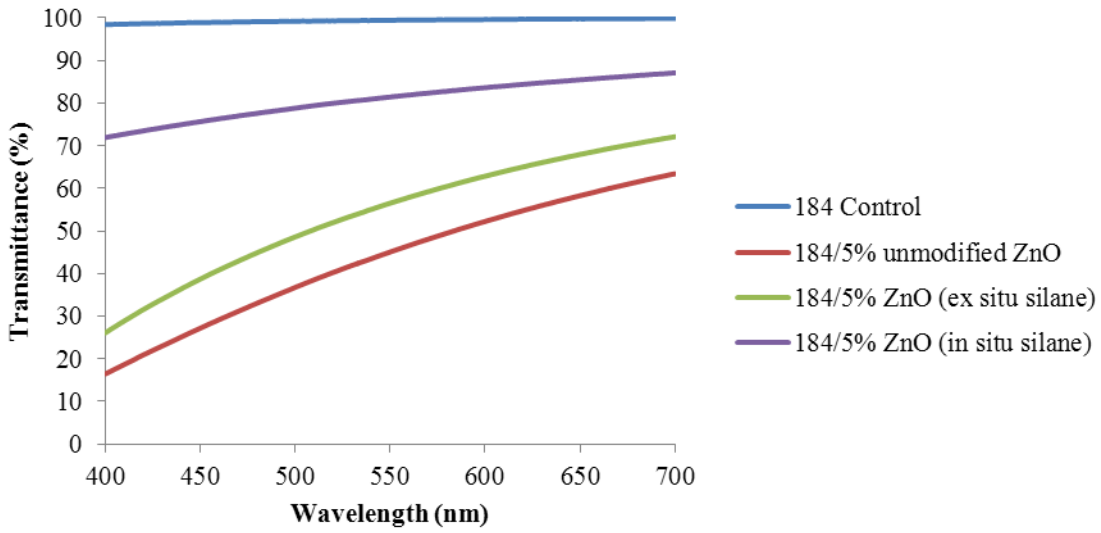

Figure 10 Transmittance spectra of silicone 184 control and silicone 184/5% ZnO nanocomposites

Figure 11 shows the extinction coefficient of silicone 184 control and silicone 184/5% ZnO nanocomposites in the visible range calculated from Beer-Lambert's law (Eq.1), where T is transmittance; k is the extinction coefficient; d is the thickness of the film; and λ is the incident wavelength.

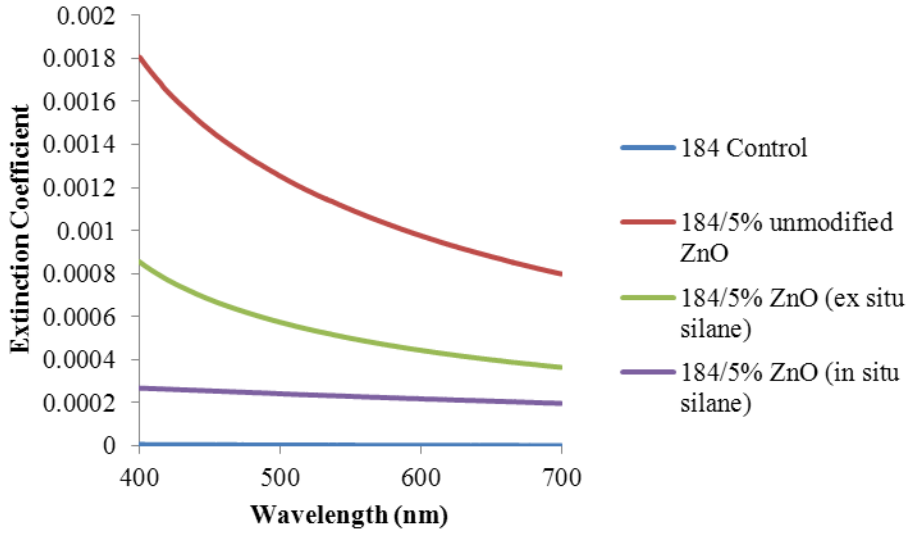

Figure 11 Extinction coefficient of silicone 184 control and silicone 184/5% ZnO nanocomposites in the visible range calculated from Beer-Lambert's law

$$T = \exp(-4\pi kd/\lambda) \qquad \text{(Eq.1)}$$

Figure 12 shows extrapolated transmittance of silicone 184 control and silicone 184/5% ZnO nanocomposites as a function of film thickness at a wavelength of 589 nm using Beer-Lambert's law (Eq.1). Transmittance of silicone 184/5% ZnO nanocomposite films at thickness between 30 and 100 microns can thus be predicted from this figure.

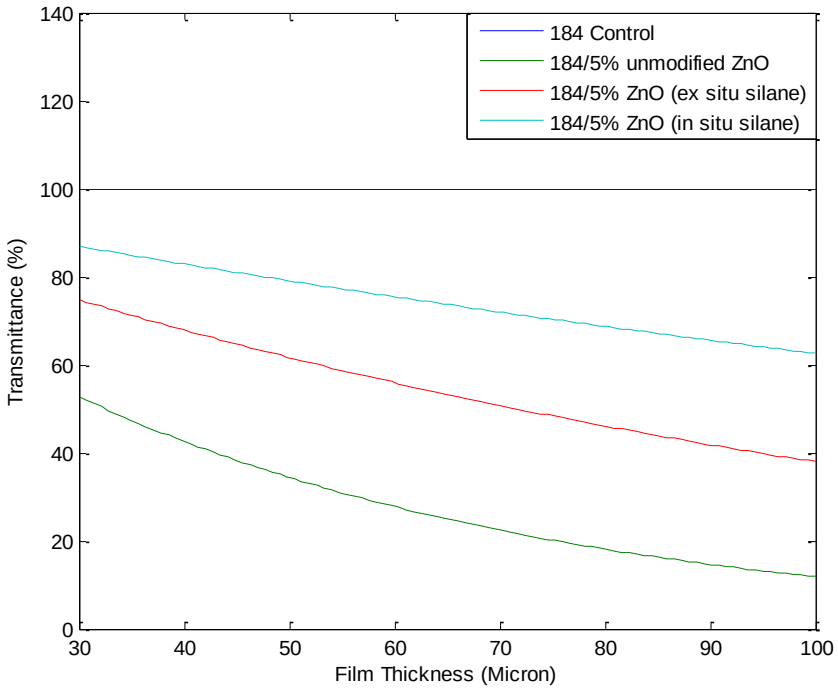

Figure 12 Extrapolated transmittance of silicone 184 control and silicone 184/5% ZnO nanocomposites as a function of film thickness at a wavelength of 589 nm

CHAPTER 4

CONCLUSION

This work reports the fabrication of stretchable and transparent silicone/ZnO nanocomposites as LED encapsulant. It was found that silane treatment would improve the dispersion of the nanoparticles and ultimately promote higher transmittance in the visible range compared with that of the silicone/unmodified ZnO nanocomposites. The silicone/5% silane-treated ZnO nanocomposite using *in situ* method exhibits elastic modulus of ~1 MPa and breaking strain of up to 160%. Collectively, these results demonstrate that the silicone/ZnO nanocomposite may serve as a promising component for future stretchable electronics.

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